PRELIMINARY RESULTS OF A STUDY OF 12 OXIDATION-RESISTANT COATINGS FOR Cb-10Ti-5Zr COLUMBIUM-ALLOY SHEET

by

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INTRODUCTION

In conjunction with development of concepts for thermal protection systems of structures for aerospace vehicles, the Langley Research Center of the National Aeronautics and Space Administration has conducted research on the protective qualities of oxidation resistant coatings for refractory metals. This research on coatings also included the effects of the coatings on the mechanical properties of the metals and the phenomena involved in oxidation protection and diffusion between coating and substrate. Preliminary results of these studies on molybdenum-alloy sheet were presented at the Sixth and Seventh Meetings of the Refractory Composites Working Group and more complete results are presented in references 1 and 2.

The data presented here are the preliminary results of an investigation of 12 oxidation resistant coatings on Cb-10Ti-5Zr columbium-alloy sheet. This study consists of screening tests which include continuous and cyclic oxidation tests at atmospheric pressure in slowly flowing air at 2000°F, 2400°F, and 2700°F and tensile stress-strain tests at room temperature, 2000°F and 2400°F. Other tests planned are continuous and cyclic oxidation tests at reduced pressures and cyclic oxidation tests at various mass flows in a 2.5 megawatt arc jet facility.

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In addition to the results of the preliminary screening tests, this report will indicate some diffusion effects for several of the coatings. More complete tensile data for temperatures from room temperature to 3000°F, are presented for sheet coated with one of the coatings.

SPECIMENS, EQUIPMENT AND PROCEDURES

All specimens utilized in this study were fabricated from annealed columbium alloy sheet with a nominal thickness of 0.020 inch. The nominal composition of the sheet was 10 percent titanium, 5 percent zirconium and the remainder columbium, by weight. The specimens were small oxidation coupons 3/4 inch by 1-1/2 inch and tensile strips 4-1/8 inch by 5/8 inch with a 2-inch reduced section 0.375 inch wide. The specimens were machined to size, tumbled in dry silicon carbide powder until the edges were rounded to a smooth radius, washed in acetone and shipped to the coating vendors. A total of 12 coatings were received from 9 vendors. Coating identifications are listed in table I.

Oxidation tests were conducted in 2 inch diameter vertical tube furnaces in air flowing at 1.5 cubic feet per hour. The dewpoint of the air was maintained below 0°F. Specimens were supported in zircon boats suspended with platinum wires. Continuous oxidation tests were performed using the weighing system described in reference 1. In the cyclic oxidation tests the specimens were inserted into the furnace and approximately 95 percent of the test temperature was achieved within 30 seconds. After one hour at temperature, the specimens were removed, weighed and visually inspected before the cycle was repeated.

Room temperature tensile tests were made in a hydraulic testing machine at nominal strain rates of 0.005 per minute to yield and 0.050 per minute from yield to failure. Strains were measured using optical strain gages which were read while the strain rate was maintained.

Elevated temperature tensile tests were performed in a screw type machine at the same strain rates previously noted. High temperature strain was measured by monitoring head motion, which was calibrated before each test to give a direct indication of specimen strain. Specimens were heated by resistance heating. Temperatures were measured using an optical pyrometer at a wave length of 0.65 microns. All temperatures reported for the tensile tests have been corrected for an assumed coating emittance of 0.8.

Phase identifications of the exterior surfaces of the coated specimens were made by X-ray diffraction methods. Metallurgical procedures were similar to those reported in reference 2. The etchant utilized in this investigation consisted of 10 parts nitric acid, 10 parts hydrofluoric acid and 30 parts lactic acid.

RESULTS AND DISCUSSION

Screening tests: A study of the weight changes occuring during the continuous oxidation tests indicated that significant coating deterioration due to Cb_2O_5 formation was associated with a weight gain of approximately 5 percent in the coupons. The times required to obtain 5 percent weight gain at 2000°F, 2400°F, and 2700°F are shown in figure 1 for the coatings investigated. Tests were terminated if 5 percent weight gain was not attained in 220 hours. The variation in life among the coatings studied is substantial. Figure 1 also indicates that most of the coatings that had long lives at the lower test temperature retained relatively long lives at the higher test temperatures.

Formation of Cb_2O_5 at failed regions caused the coating to spall off the specimens along the edges. This was the mechanism of failure for all specimens in the cyclic oxidation tests. These edge failures were easily detectable by visual inspection.
Times to visual coating failure at 2000°F, 2400°F and 2700°F are shown in figure 2. Again, tests were terminated after 220 hours if failure had not occurred. The reduction in life obtained in the cyclic tests was considerably less than that obtained for molybdenum alloy with a silicide-base coating, noted in reference 1. As noted herein for the continuous tests, the coatings that showed longest lives at 2000°F in the cyclic tests also performed similarily in the 2400°F cyclic tests. Lifetimes in the cyclic tests at 2700°F were generally short for all the coatings investigated.

Room temperature tensile properties are shown in figure 3 for the specimens in the as-coated condition and after 1 and 8 hour exposures in air at 2400°F. Coatings which failed by oxidation during the exposures are indicated by zero tensile strength in figure 3. Several coatings which provided relatively long lives for the columbium alloy specimens (figures 1

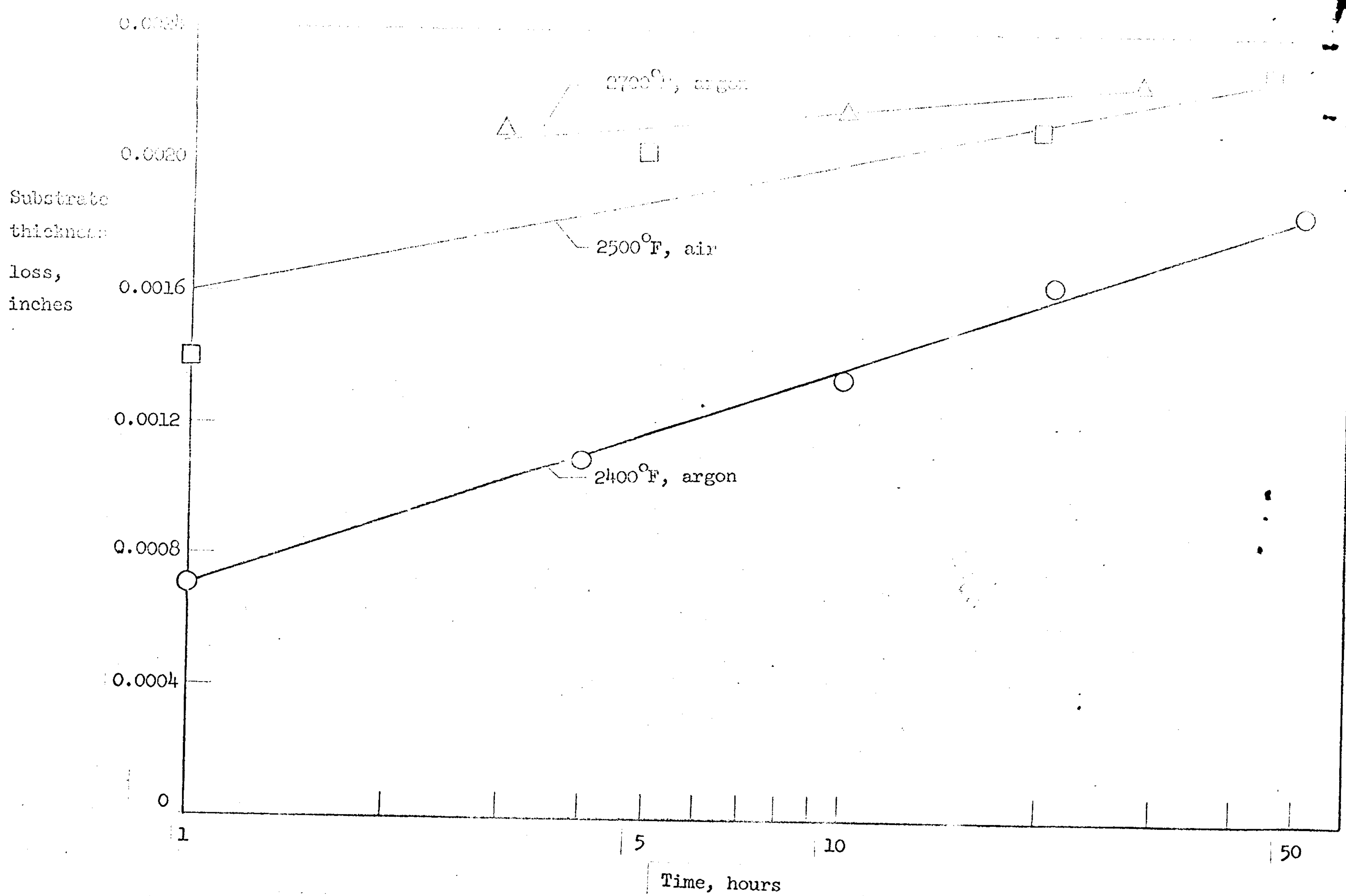

Figure 10. – Loss of substrate thickness as a function of time at several temperatures for columbium alloy sheet with coating 12.

[illegible] 2) had embrittling effect on the substrate indicated by a low value of elongation in figure 3.

Tensile properties for coated columbium alloy sheet at 2000°F and 2400°F are shown in figure 4 for each of the coatings investigated. At 2000°F the coated specimens exhibited tensile strengths from 22 to 45 ksi with elongations of 0 to 28 percent. At 2400°F the tensile strength of the coated specimens ranged from 11 to 19 ksi with elongations of 4 to 38 percent.

Tensile tests on coating 12: A more comprehensive study of the variation of tensile properties with temperature for the columbium alloy sheet with coating 12 was made and the results are shown in figures 5, 6, and 7. Figure 5 presents tensile data at room temperature and at temperatures from 1600°F to 3000°F. The relatively low value of elongation obtained at [illegible]°F for the columbium alloy in this study is in agreement with low values indicated in other published data for columbium alloys in the 1200°F to [illegible]°F temperature range. The presence of the coating generally decreases the value of elongation obtained in the tensile tests. The low value of elongation obtained at 3000°F is probably the result of the resistance [illegible] techniques used in this study. At 2500°F the coated columbium-alloy sheet exhibited short time tensile strength of approximately 10 ksi with approximately 27 percent elongation.

Figures 6 and 7 show tensile properties of the coated columbium alloy at room temperature and 2500°F, respectively, after various exposure times in air at 2500°F. After 20 hours exposure at 2500°F the coated sheet had room temperature tensile strength of 83 ksi with 3 percent elongation and at 2500°F tensile strength of 16 ksi with 16 percent elongation. However, after 60 hours exposure at 2500°F the coated columbium alloy had zero elongation at room temperature.

An examination of the factors which contribute to the brittleness of the material is in progress. As will be noted subsequently, only a slight loss of substrate thickness with time at temperatures from 2000°F to 2700°F was observed for the columbium alloy with coating 12. This indicates that the embrittlement encountered will not be detected by ordinary metallographic inspection of etched, sectioned specimens. In addition, preliminary microhardness traverses did not reveal definitive information. For these reasons, it appears that mechanical tests are required to determine embrittling effects of exposure for coated columbium alloys.

Metallography and Diffusion: The microstructure of the columbium alloy sheet before coating and after coating with several of the coatings investigated is shown in figure 8. In considering these microstructures, recall that the uncoated sheet exhibited 30 percent elongation at room temperature whereas the sheet with coatings 2, 6, 11, and 12 at room temperature exhibited elongation values of 0, 2, 14, and 14 percent, respectively. It is evident that the appearance of relatively heavy concentrations of precipitates in the structure is not an automatic indication that the structure has been severely embrittled. The composition of the precipitates appears to be of significance but has not been determined to date. Studies of these precipitates by electron probe microanalysis and vacuum fusion analysis are in progress at the Langley Research Center.

The magnitude of substrate thickness loss by diffusion as measured by optical techniques on sectioned, etched specimens is indicated in figure 9 for several of the coatings investigated at 2400°F and in figure 10 for coating 12 at 2400°F, 2500°F, and 2700°F. These data are of general interest. However, as was noted in the preceeding section, the loss of substrate in the coated columbium-alloy sheet is one of several effects that apparently influence the ductility of the columbium-alloy sheet.

CONCLUDING REMARKS

The following conclusions are made on the basis of the preliminary data presented here for coated Cb-10Ti-5Zr columbium-alloy sheet with respect to its possible usefulness in aerospace vehicles:

(1) Useful oxidation lifetimes and tensile properties can be retained by coated columbium alloy sheet for applications in thermal protection systems up to 2500°F.

(2) Satisfactory mechanical properties were obtained for coated columbium alloy sheet after high temperature exposure in air for moderate times. For example, tensile strength of 82 ksi with 3 percent elongation was found at room temperature after 20 hours exposure at 2500°F. However, after 80 hours exposure at 2500°F, the coated columbium alloy had zero elongation.

(3) Ordinary metallographic examination does not reveal the extent of the embrittlement encountered during the coating process or subsequent, elevated temperature exposures. Mechanical tests appear necessary to measure the extent of the embrittlement.

REFERENCES

1. Rummler, D. R., Stein, B. A., and Pride, R. A.: A Study of Several Oxidation Resistant Coatings on Mo-0.5Ti Alloy Sheet at 2500°F. NASA TN D-2040, 1964.

2. Stein, B. A. and Lisagor, W. B.: Diffusion Studies of Several Oxidation Resistant Coatings on Mo-0.5Ti Molybdenum Alloy at 2500°F. NASA TN D-2039, 1964.

TABLE I — IDENTIFICATIONS OF COATINGS INVESTIGATED FOR A COLUMBIUM ALLOY SHEET (a)

Coating Designation	Supplier, Designation	Coating Thickness, Inch	Method of Application	Predominent Composition of Coating Surface (b)
1	American Machine and Foundry Co., AMF Kote 3	0.0015	2 cycle pack cementation	$Cb\ B_2$
2	American Machine and Foundry Co., AMF Kote 30	0.0031	3 cycle pack cementation	$Cb\ B_2$
3	Chance Vought Corp.	0.0020	2 cycle pack cementation; first cycle silicon; second cycle chromium-bornn	$Cb\ Si_2$
4	Boeing Co., Disil 1	0.0015	1 cycle fluidized bed	$Cb\ Si_2$
5	Boeing Co., Disil 2	0.0015	1 cycle fluidized SiC overlay on 1 side	$Cb\ Si_2$, SiC (c)
6	Dupont Co., 1	0.0016	First cycle vapor deposited titanium-chromium; second cycle fluidized bed modified silicide	$Cb\ Si_2$ $Cr\ Si_2$ (d)
7	Dupont Co., 2	0.0008	First cycle vapor deposited titanium-chromium; second cycle fluidized bed modified silicide	$Cb\ Si_2$
8	General Telephone and Electronics Co., Sylcor	0.0034	2 cycle pack cementation; first cycle titanium; second cycle silicon	$Cb\ Si_2$

9	General Technologies Corp.	0.0024	3 cycle pack cementation; first cycle chromium-titanium; second and third cycles silicon, carbon, carbon, tantalum	$Cb\ Si_2$ $Cr\ Si_2$ (d)
10	North American Aviation, Inc.	0.0013	1 cycle aluminide	Al_3Cb
11	Pfaudler Co.	0.0031	1 cycle pack cementation; alloyed silicide	$Cb\ Si_2$
12	TAPCO	0.0020	2 cycle pack cementation; first cycle prealloyed chromium-titanium; second cycle silicon	$Cb\ Si_2$ $Cr\ Si_2$ (d)

(a) All coatings were applied on 0.020 inch-thick D-36 columbium-alloy sheet (Cb -10Ti-5Zr)

(b) Identified by X-ray diffraction procedures

(c) Thin layer of SiC over $CbSi_2$

(d) Solid solution of the compounds

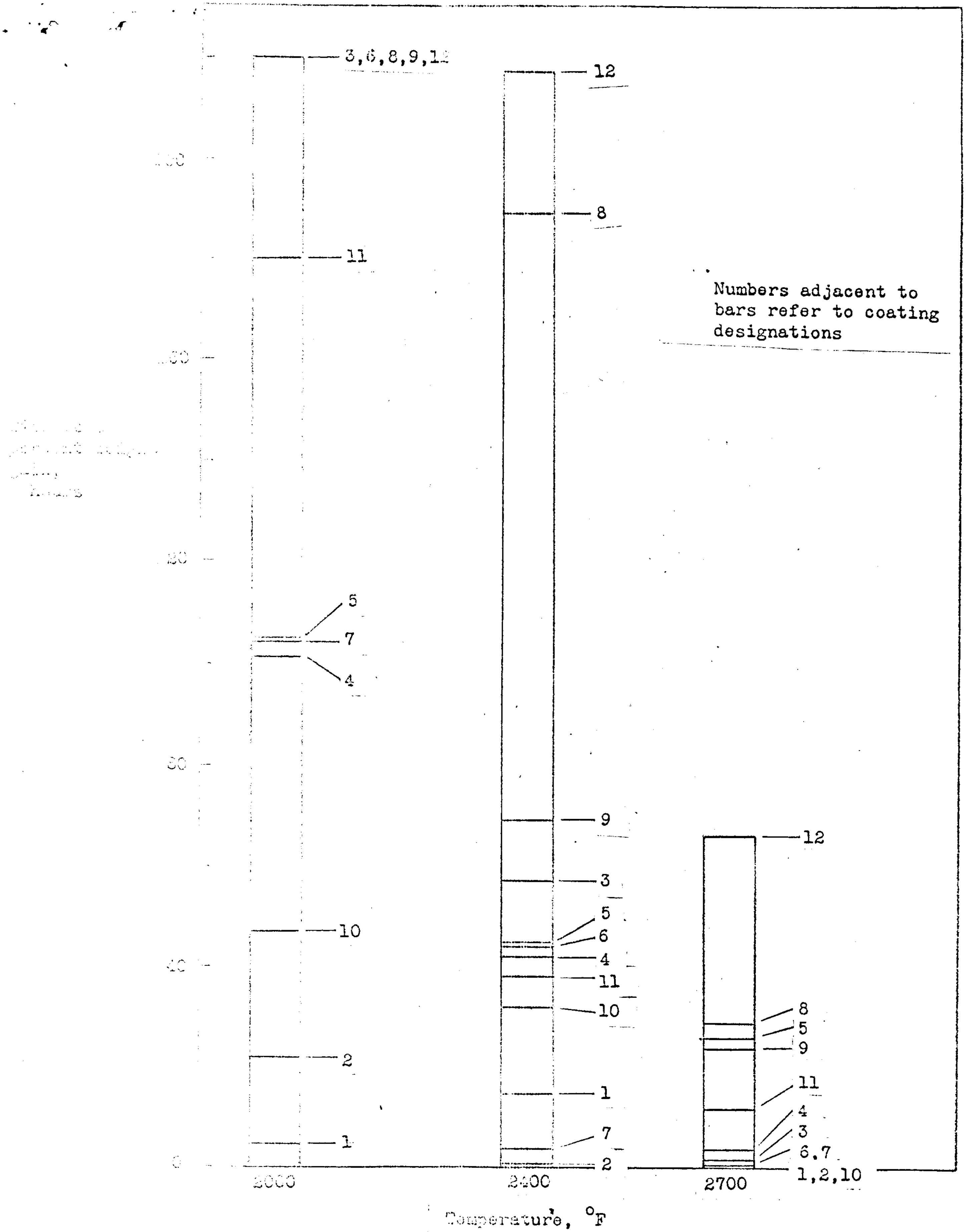

Figure 1. - Time to 5 percent weight gain in continuous oxidation tests as a function of temperature for 12 oxidation resistant coatings on columbium alloy sheet

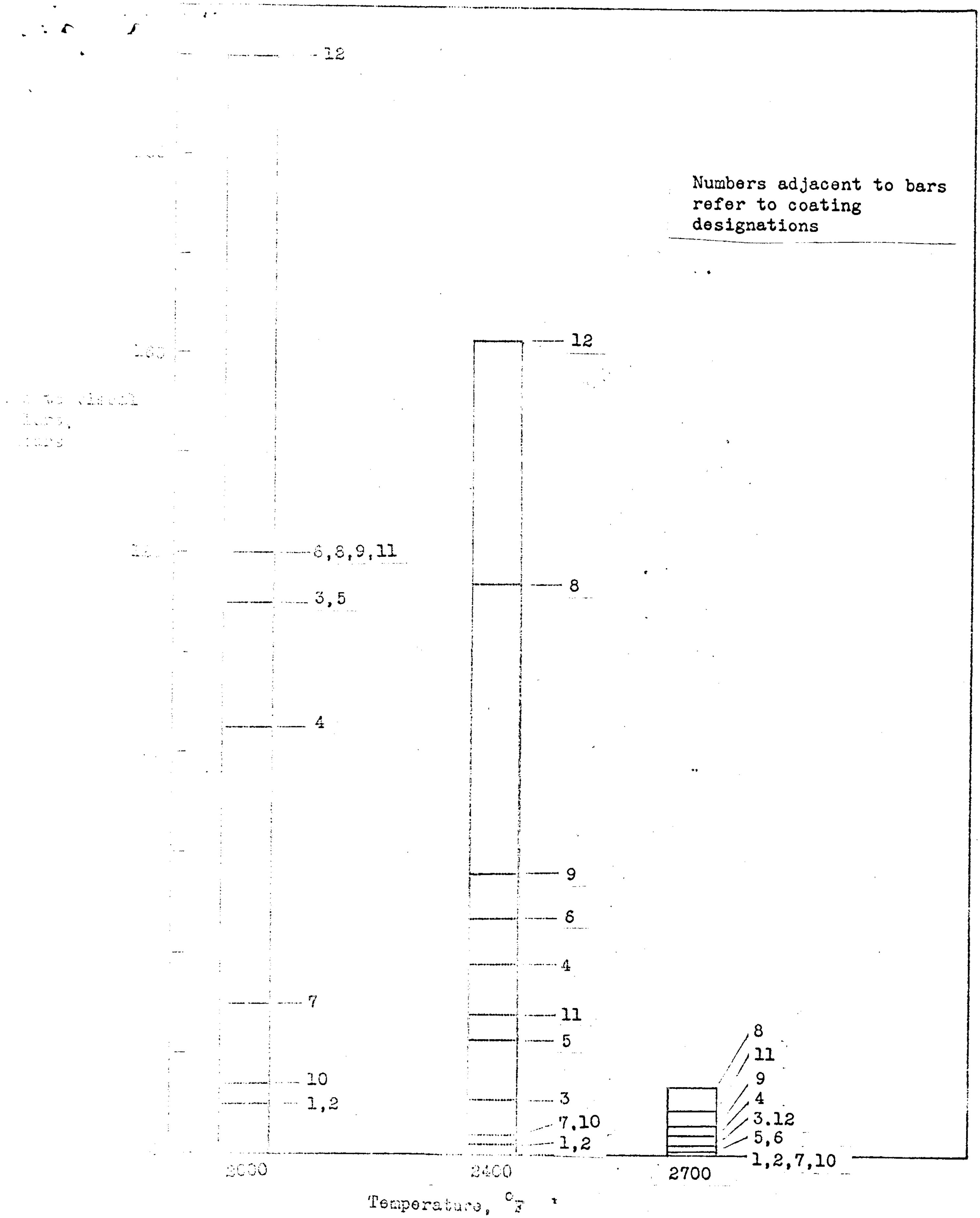

Figure 2. – Time to visual failure in cyclic oxidation tests as a function of temperature for 12 oxidation resistant coatings on columbium alloy sheet.

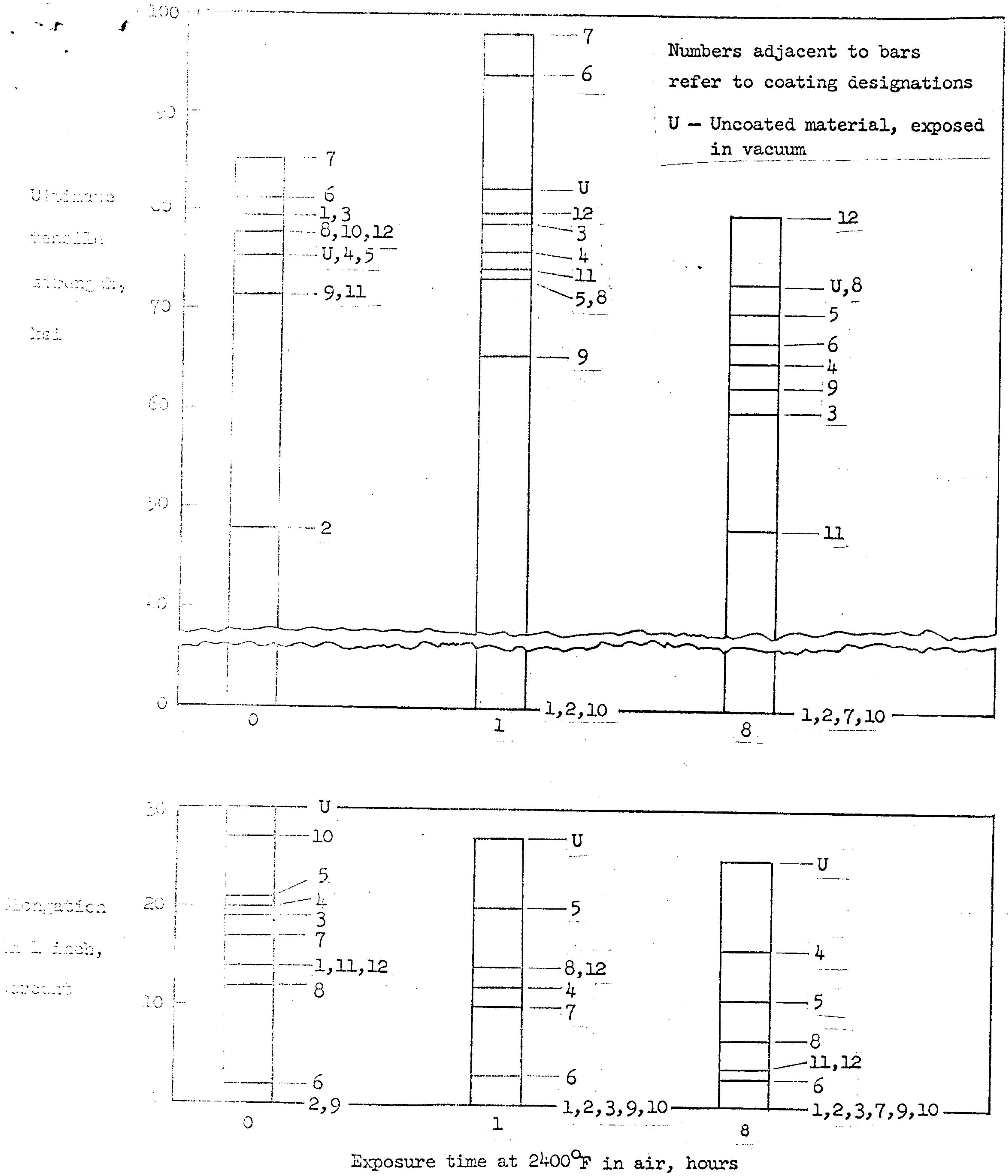

Figure 3. – Room temperature tensile properties of columbium alloy sheet with 12 oxidation restant coatings. Uncoated specimens (U) were exposed in vacuum.

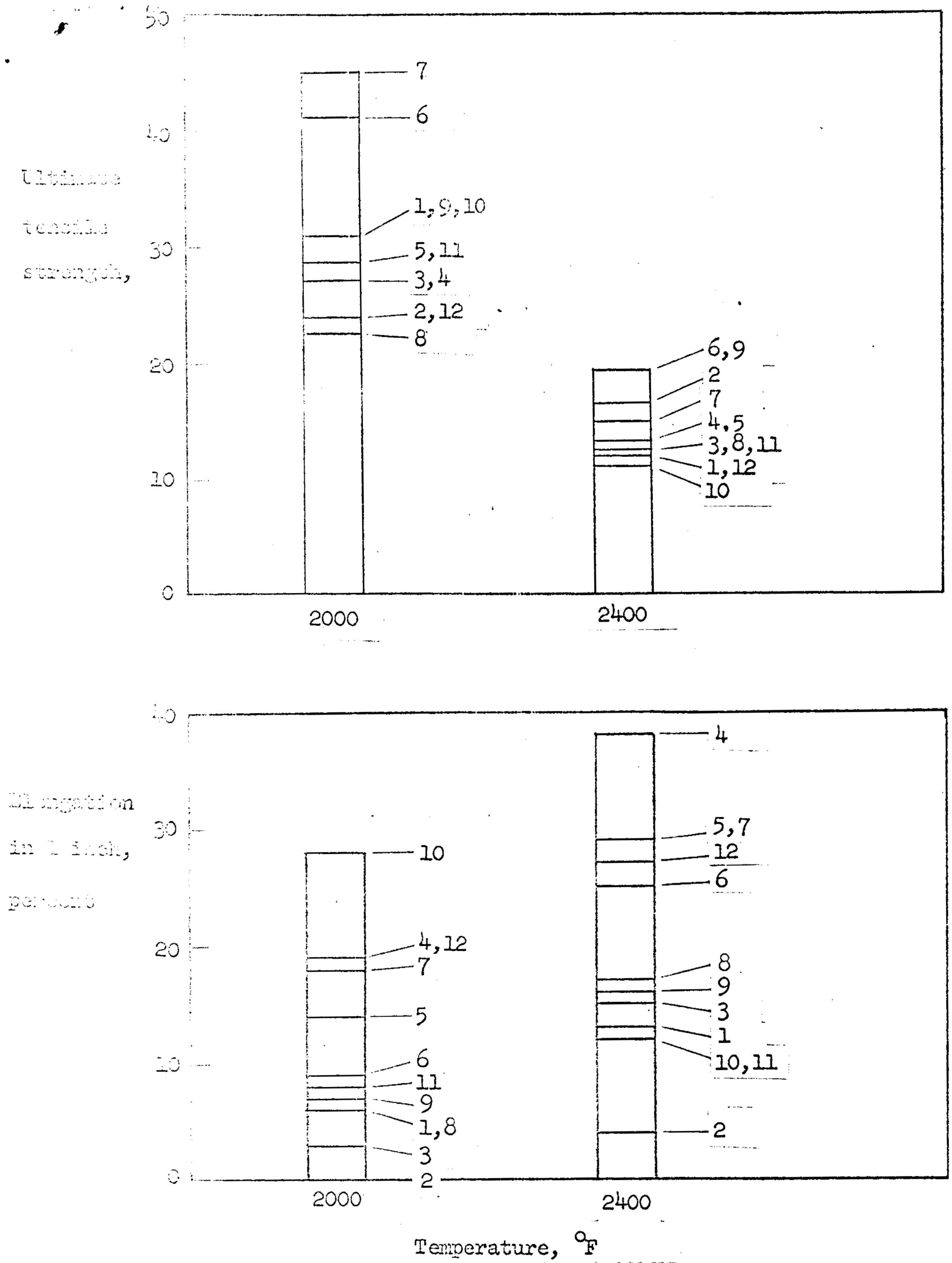

Figure 4. – Tensile properties of columbium alloy sheet with 12 oxidation resistant coatings at 2000°F and 2400°F in air.

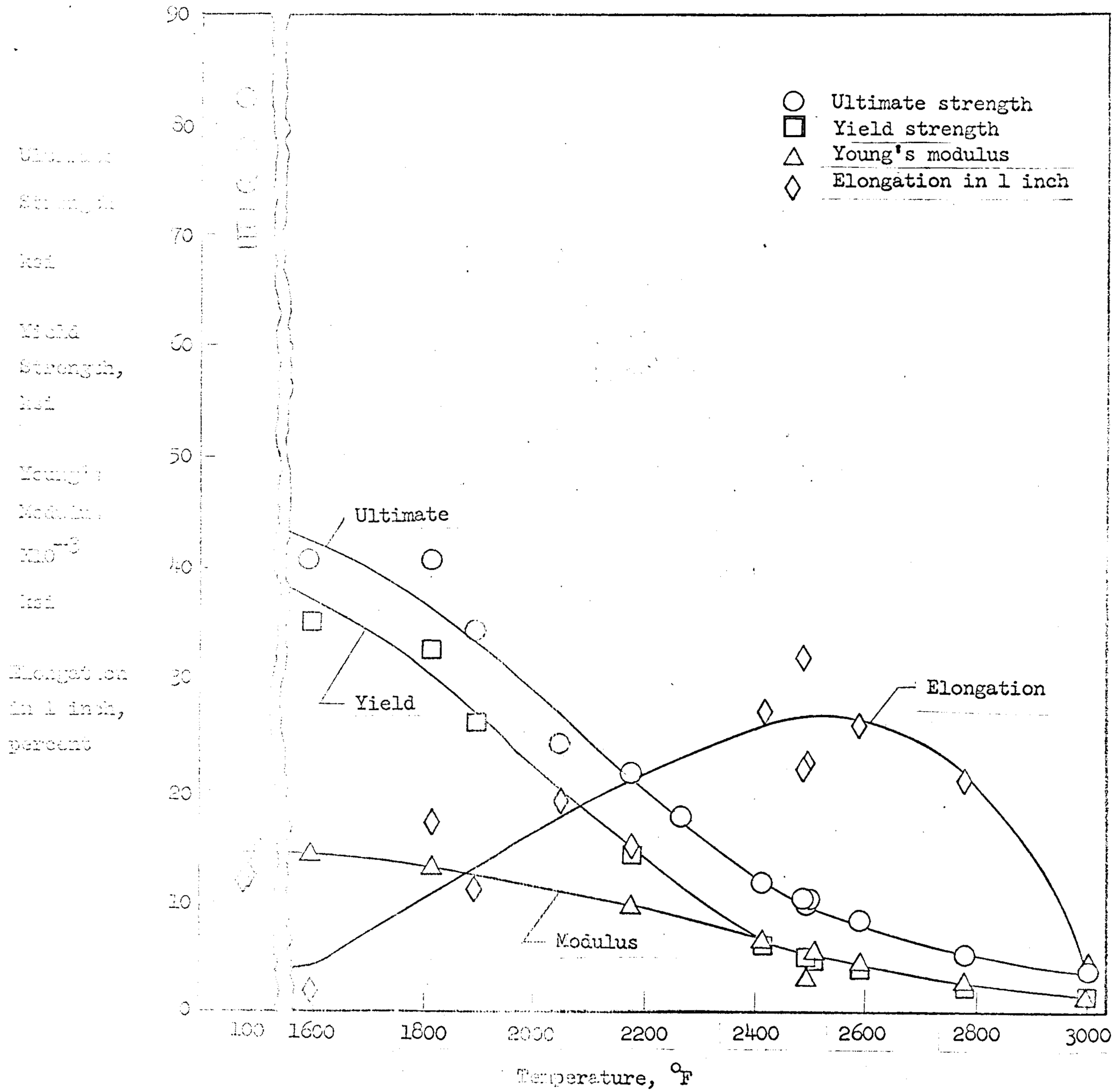

Figure 5. – Variation of tensile properties with temperature for columbium alloy sheet with coating 12.

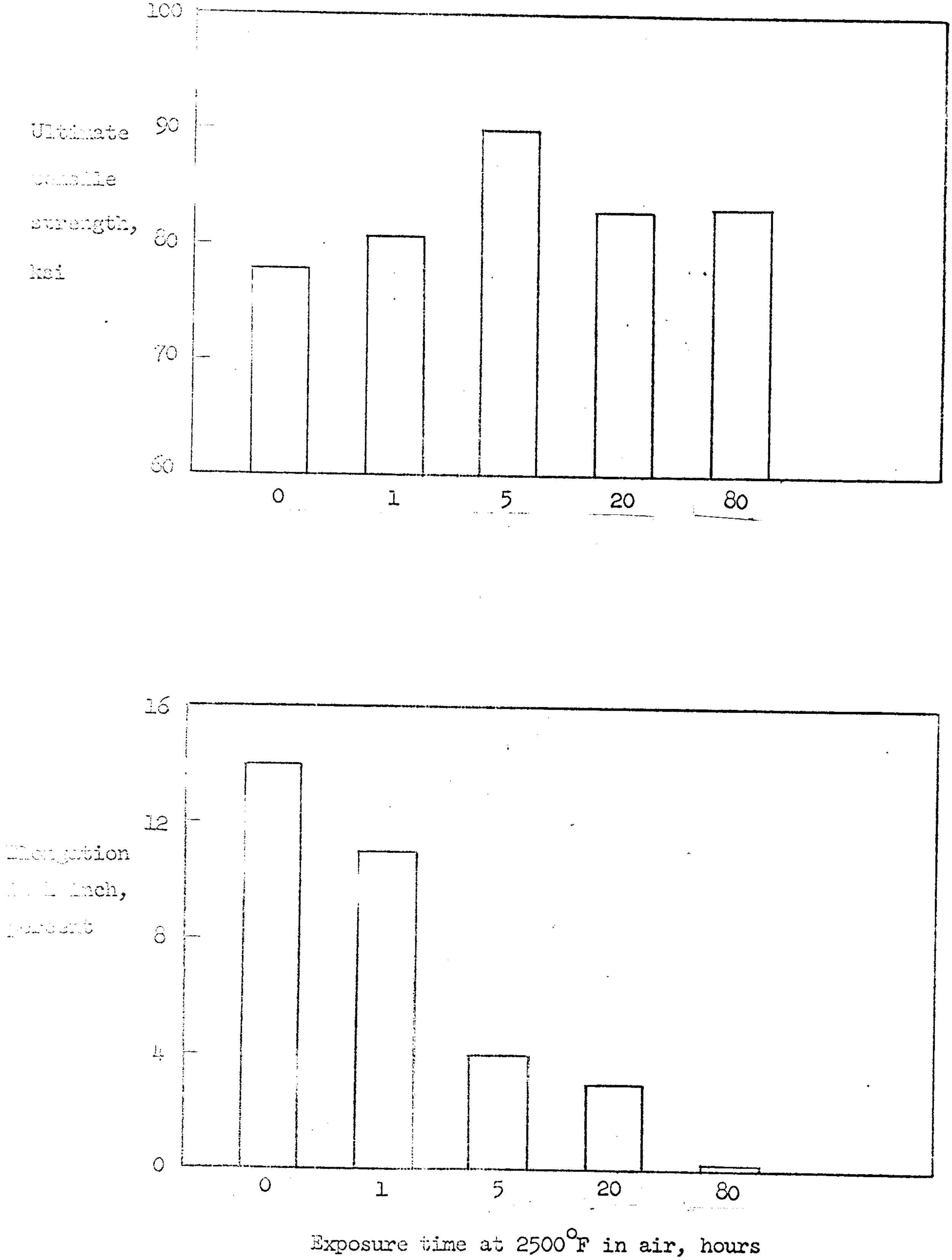

Figure 6. – Room temperature tensile properties of columbium alloy sheet with coating 12 after various exposures at 2500°F in air.

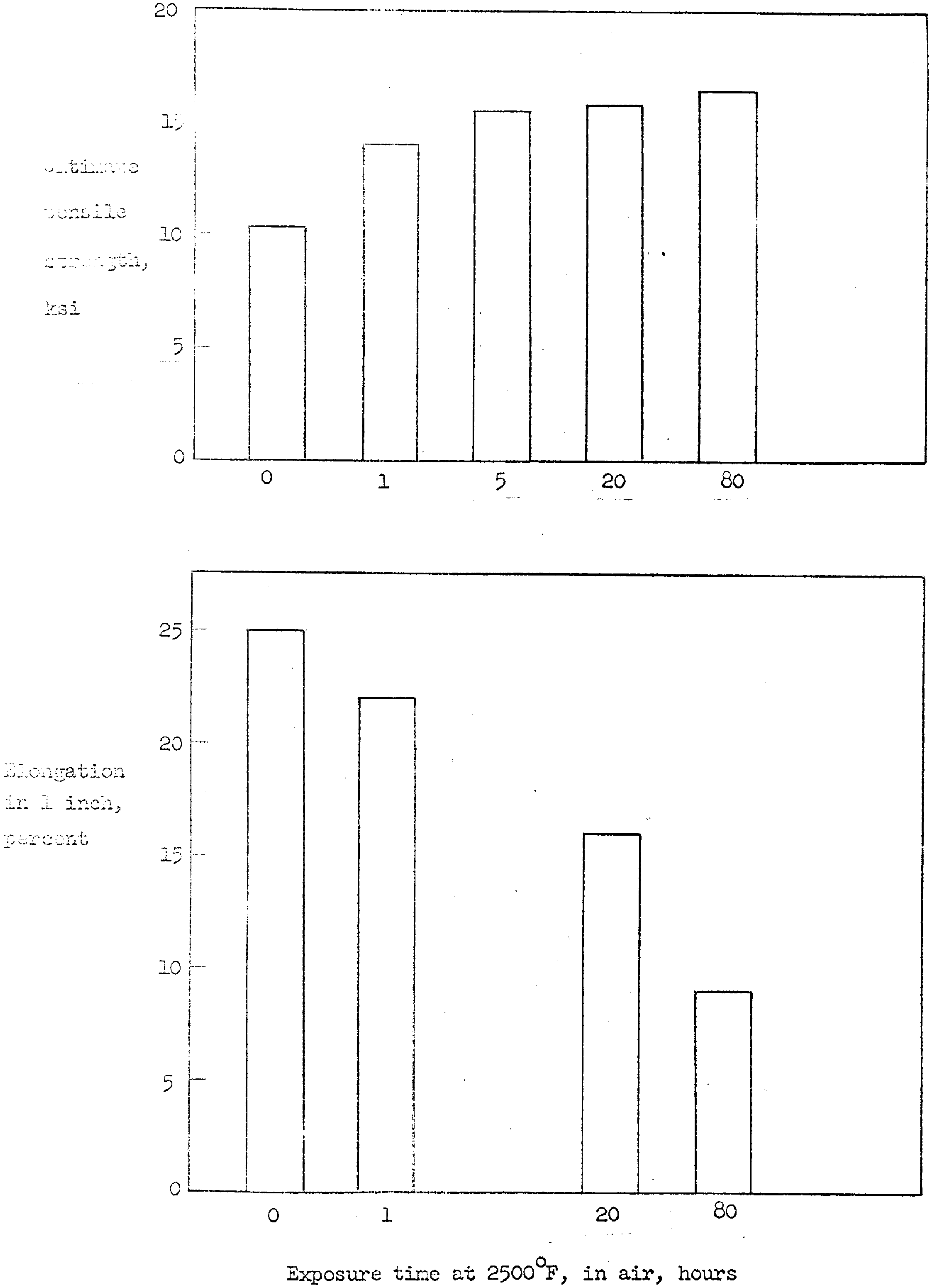

Figure 7. – Tensile properties of columbium alloy sheet with coating 12 at 2500°F after various exposures at 2500°F in air.

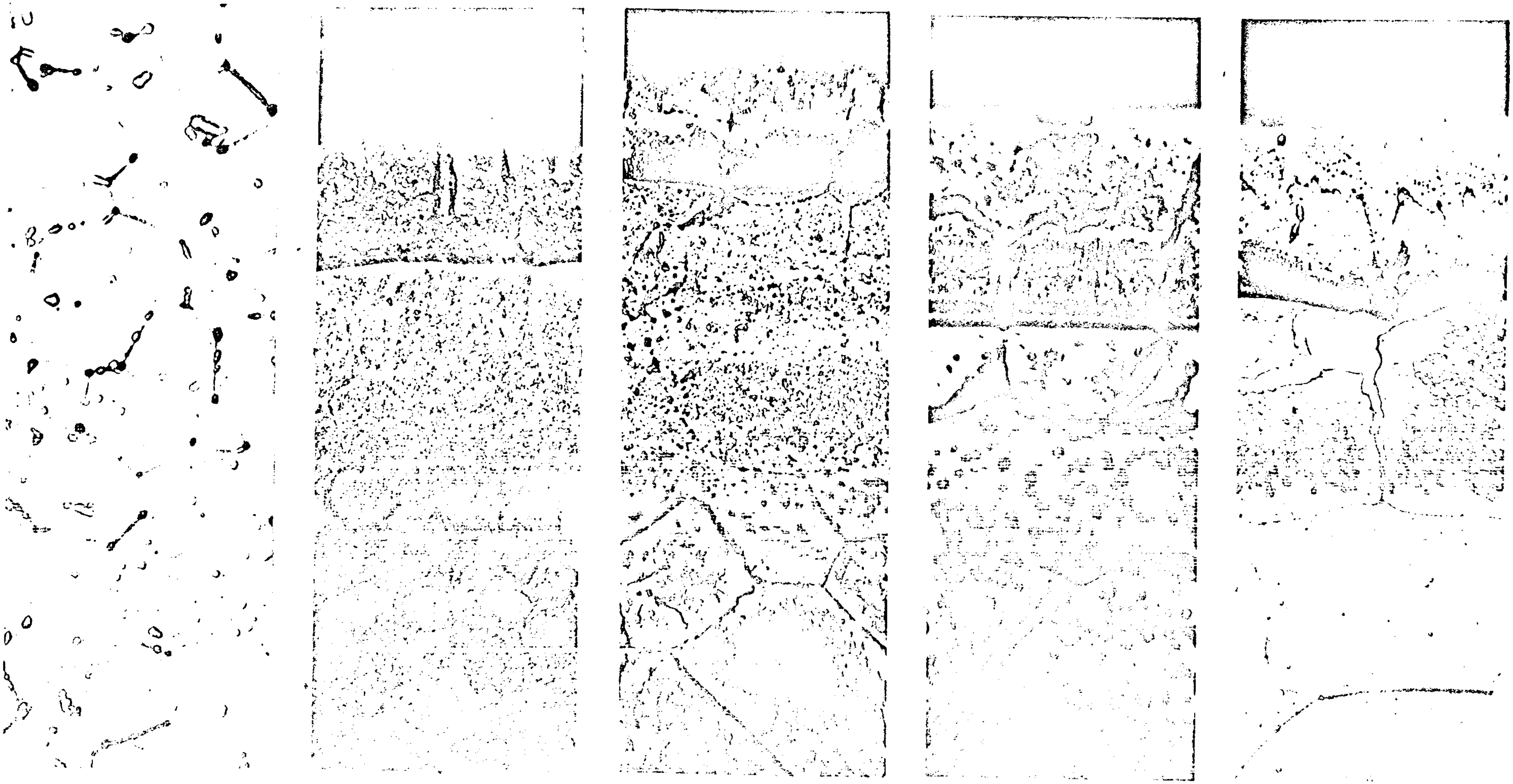

Figure [illegible]. [illegible] of columbium alloy with several coatings in [illegible] condition. X500

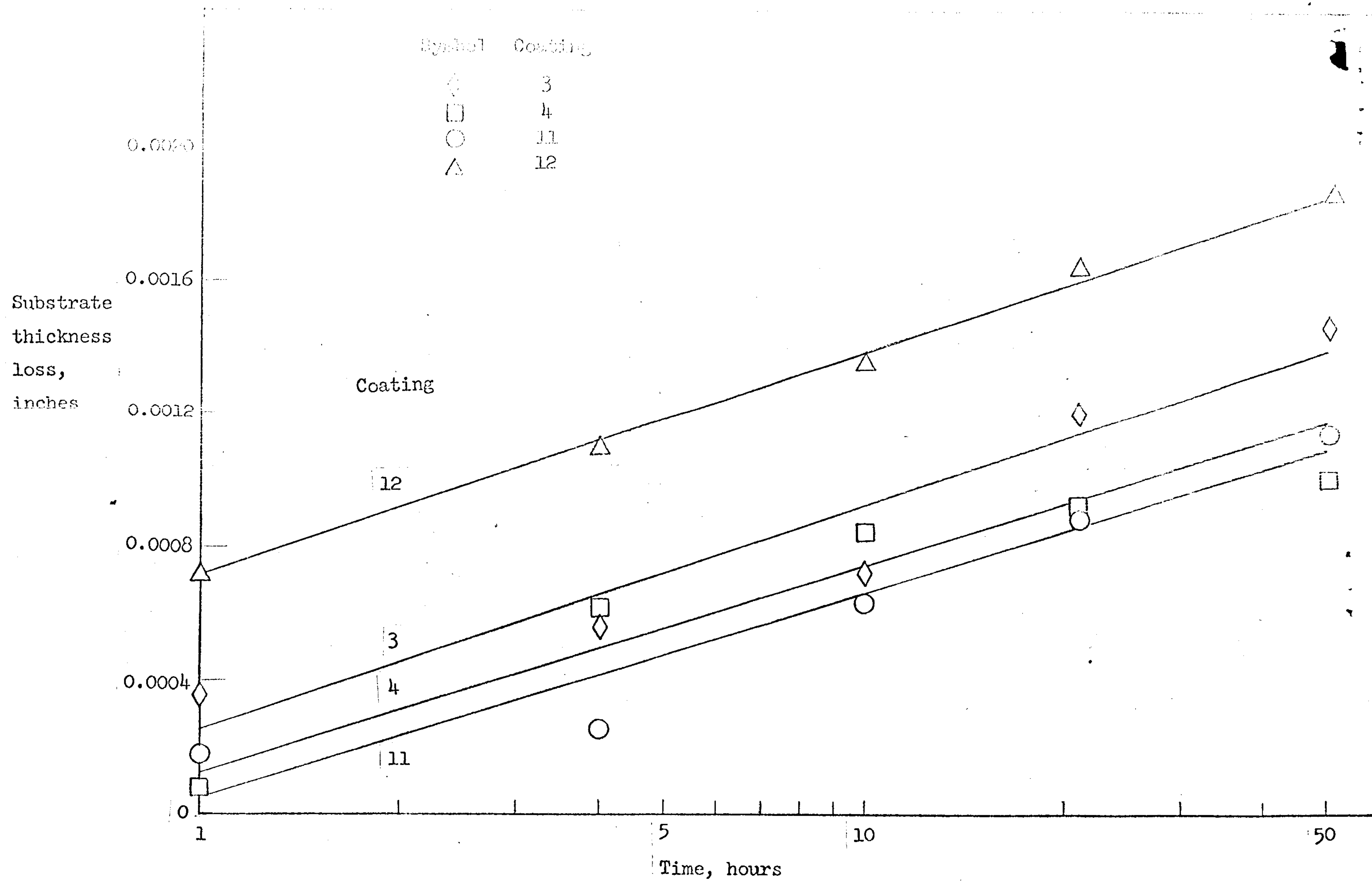

Figure 9. - Loss of substrate thickness as a function of time at 2400°F in argon for columbium alloy with several coatings.